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(54) METHOD AND APPARATUS FOR MAKING HIGH STRENGTH METALS WITH A FACE-CENTERED-CUBIC STRUCTURE

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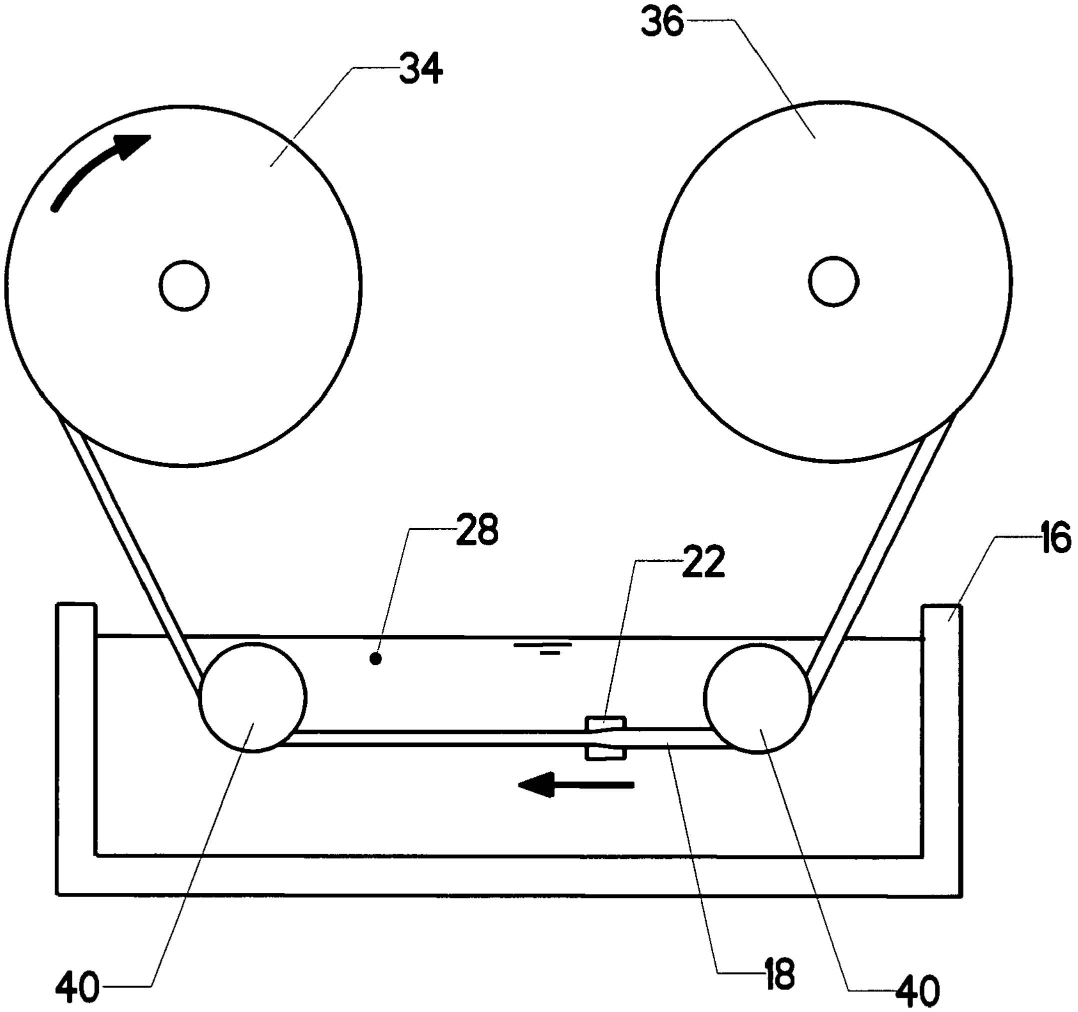
(57) **ABSTRACT**

A process for increasing the strength of pure copper and other fcc matrix alloys. The method is particularly applicable to face-centered-cubic materials that undergo dynamic recovery when strain-hardened at room temperature. A cryogenic strain hardening process is used to create a high strength pure copper or copper+Al_2O_3 alloy. The strength of the material is substantially increased. However, the loss of conductivity is minimal. In the preferred embodiment, pure copper or a copper alloy is drawn into a wire at a temperature of about 77 K. Dynamic recovery of the material is substantially reduced. With this method, drawn copper wire exhibits a strength level about 45% higher than that achievable by an equivalent room temperature deformation.



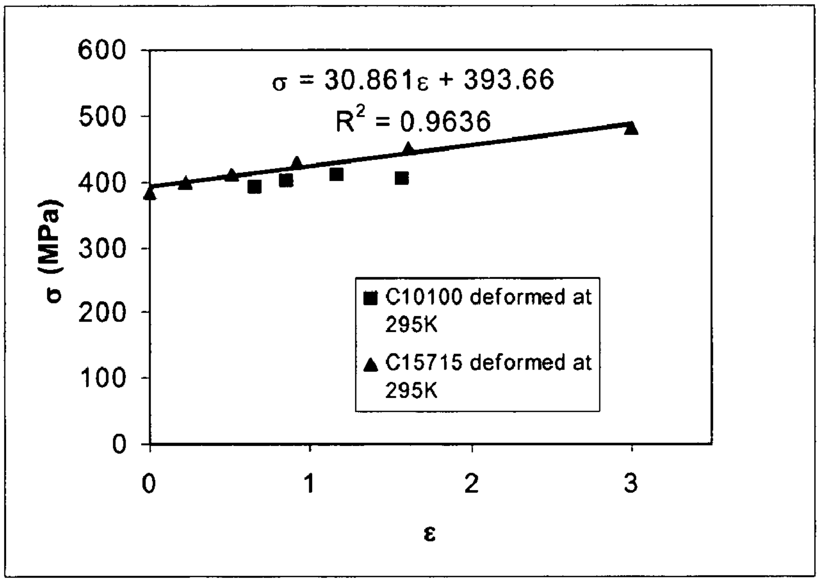

σ = 30.861ε + 393.66
R² = 0.9636
σ (MPa)
600
500
400
300
200
100
0
0
1
2
3
ε
■ C10100 deformed at 295K
▲ C15715 deformed at 295K

FIG. 1

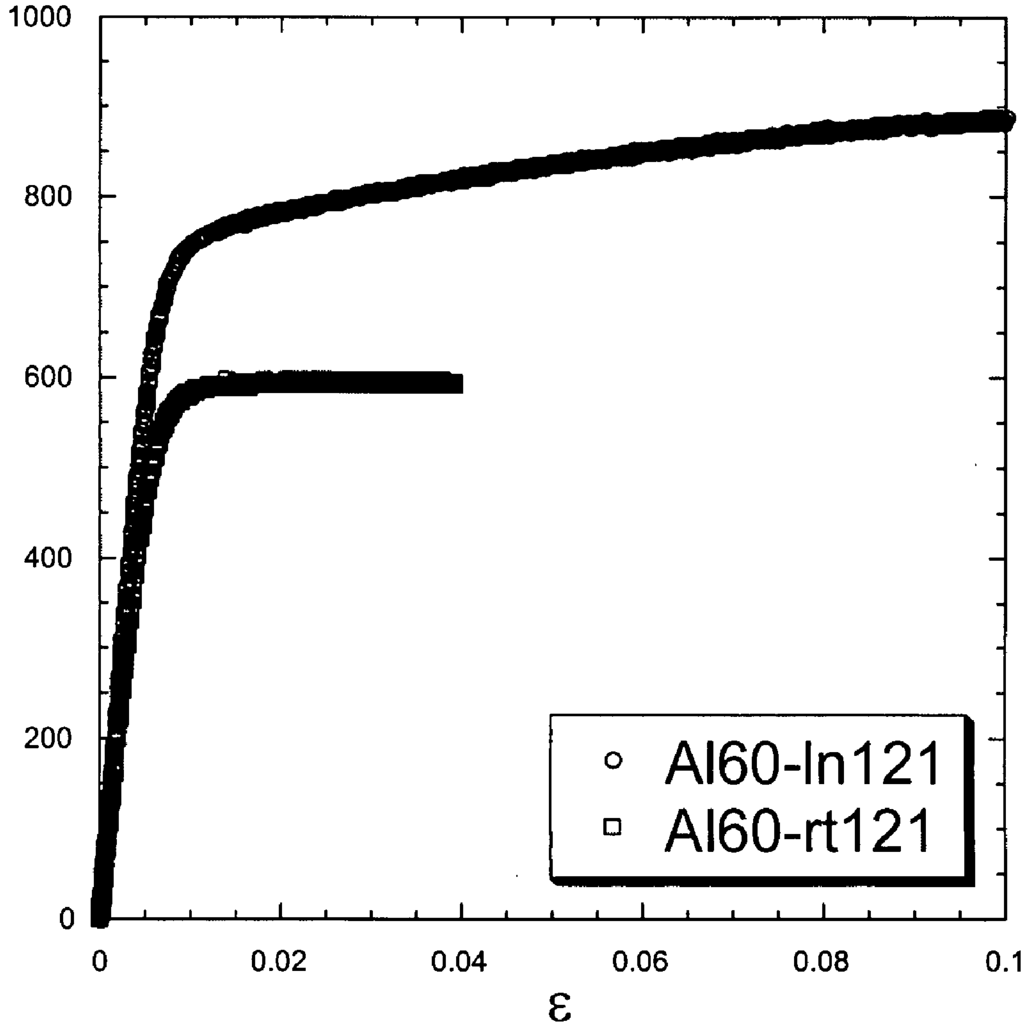
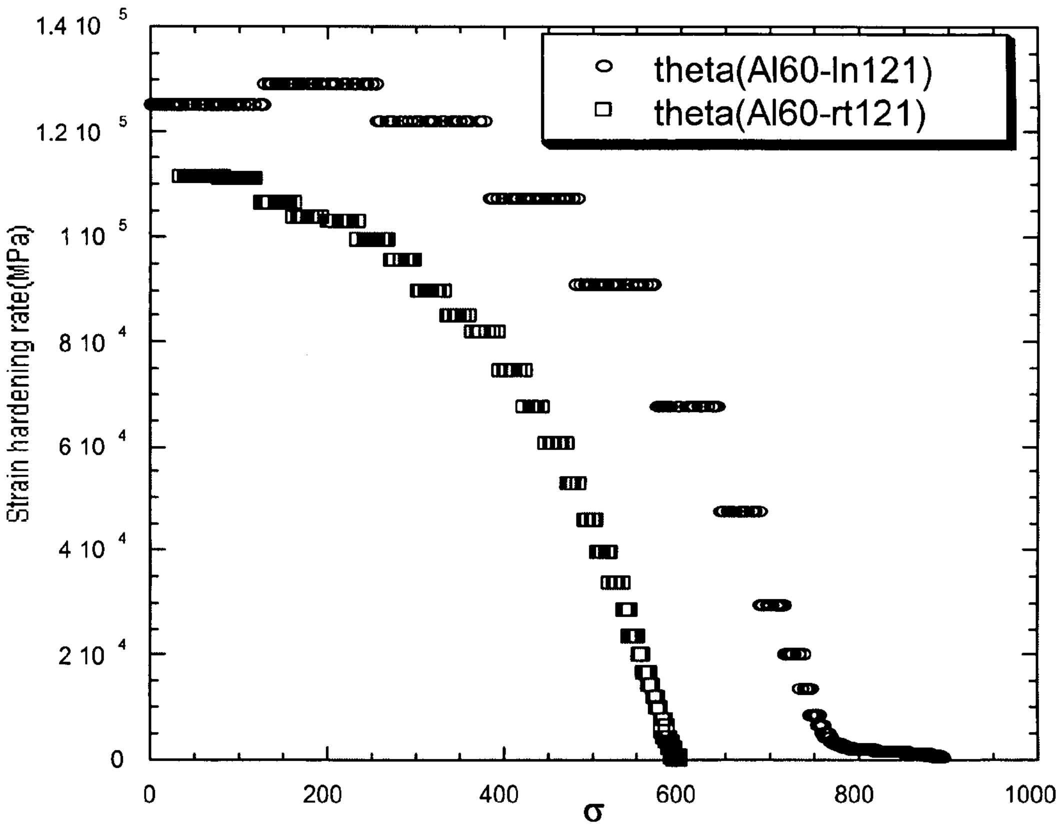

1000
800
600
400
200
0
0
0.02
0.04
0.06
0.08
0.1
ε
○ Al60-In121
□ Al60-rt121

FIG. 2



1.4 10 5
1.2 10 5
1 10 5
8 10 4
6 10 4
4 10 4
2 10 4
0
Strain hardening rate(MPa)
0
200
400
600
800
1000
σ
○ theta(Al60-In121)
□ theta(Al60-rt121)

FIG. 3

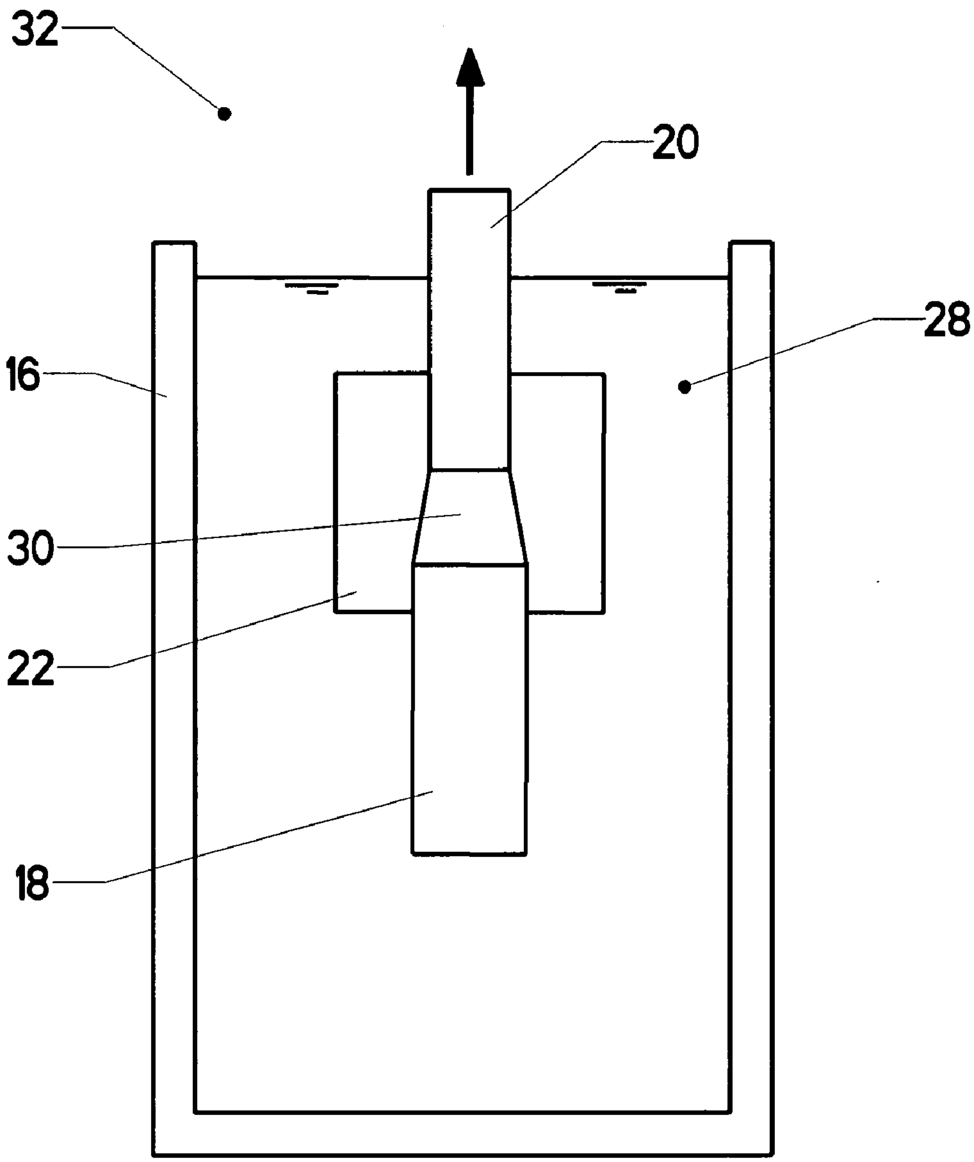


FIG. 4

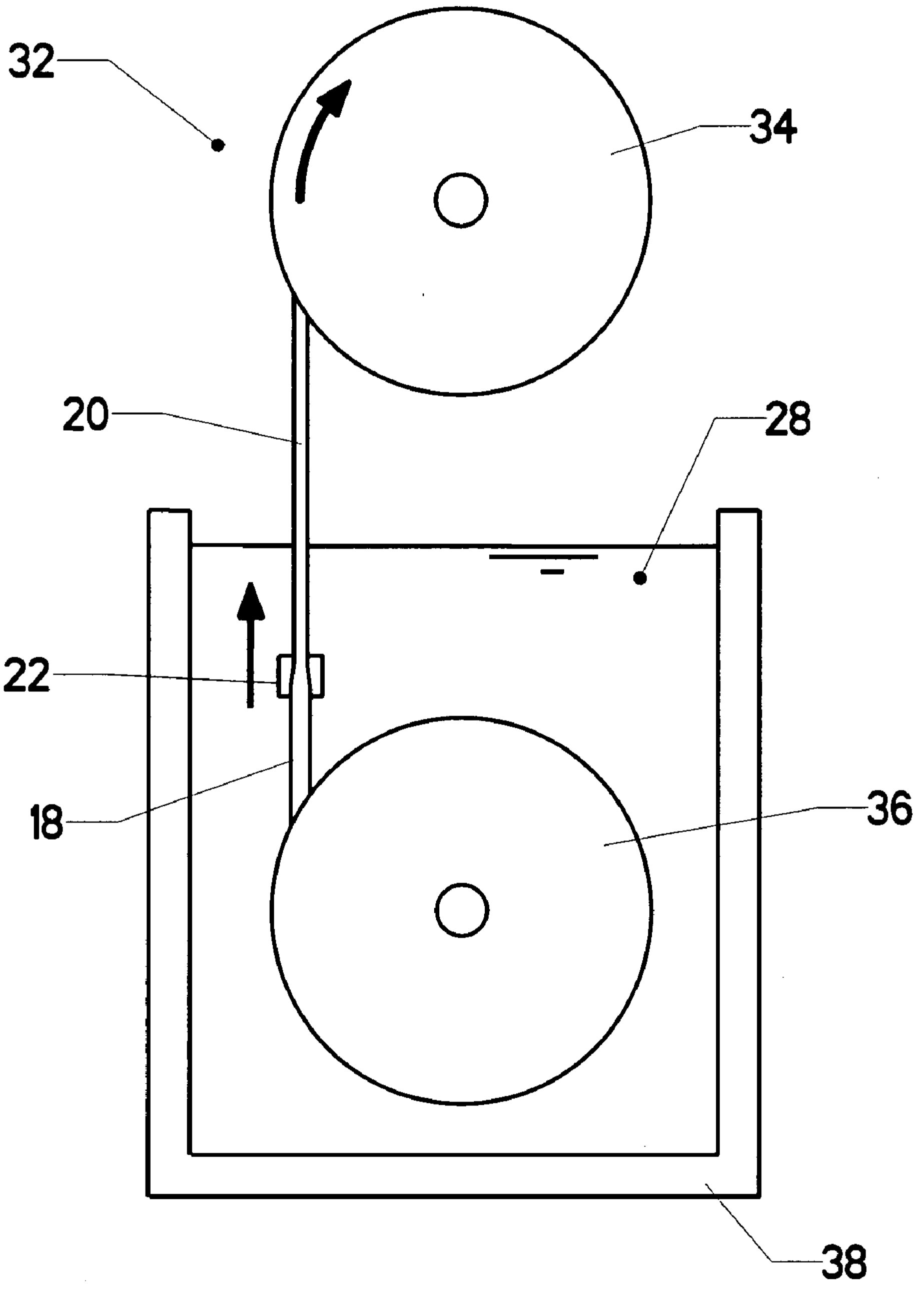


FIG. 5

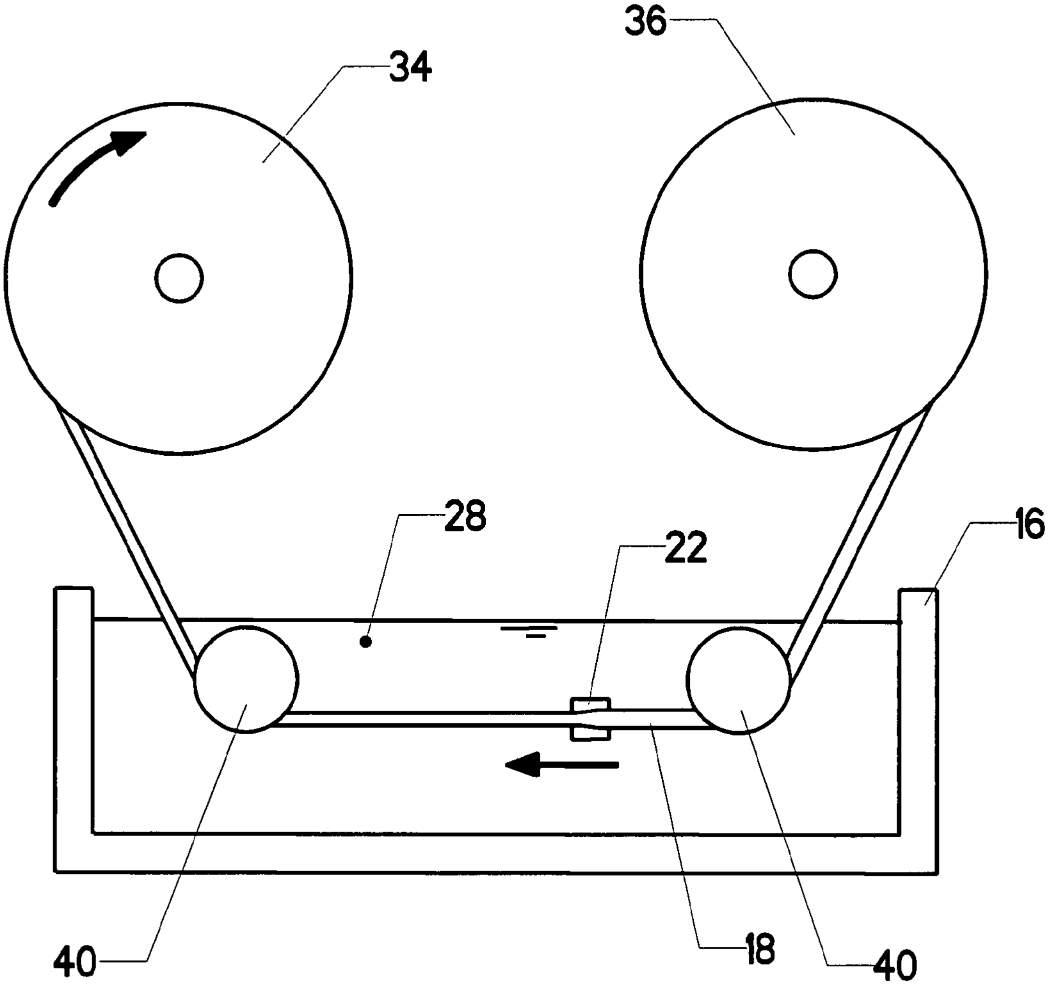


FIG. 6

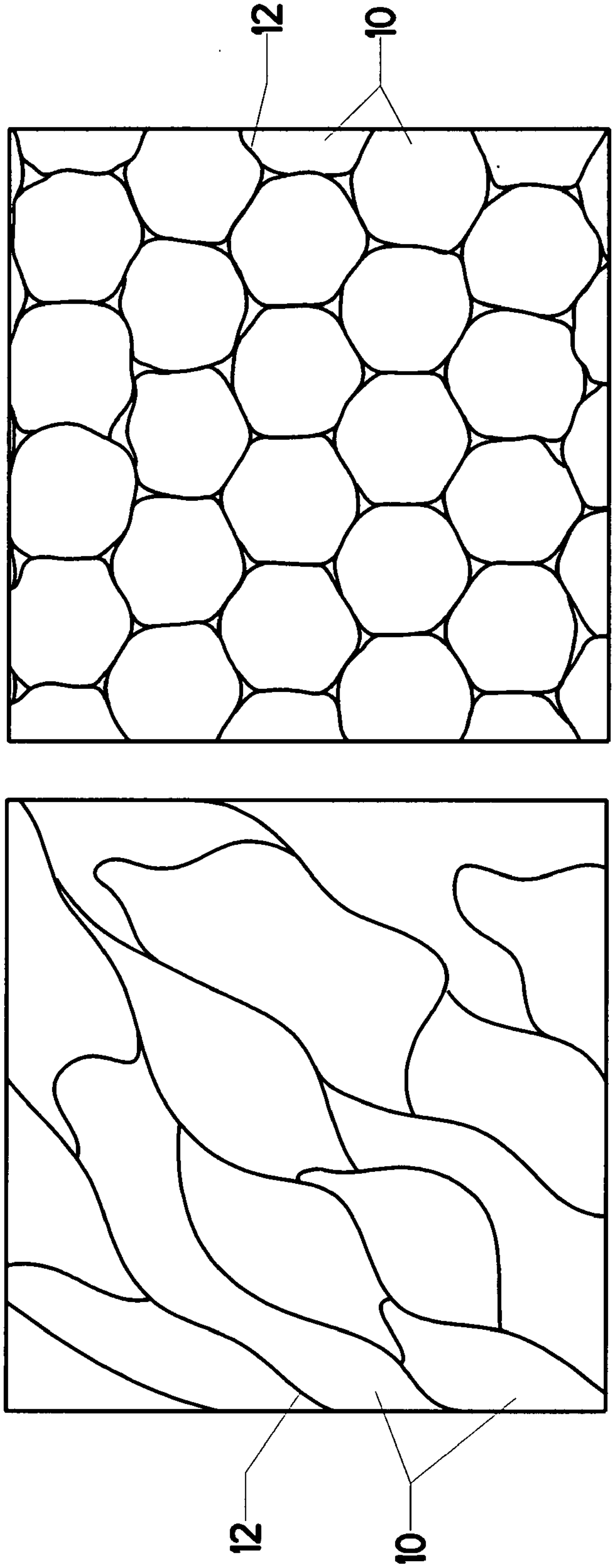


FIG. 7

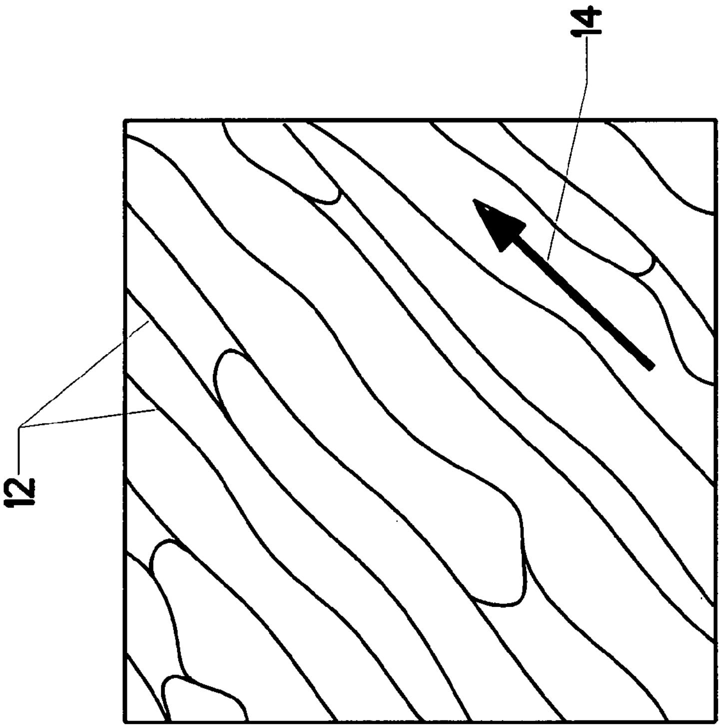


FIG. 8

METHOD AND APPARATUS FOR MAKING HIGH STRENGTH METALS WITH A FACE-CENTERED-CUBIC STRUCTURE

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] This invention relates to the field of materials. More specifically, the invention comprises a method and apparatus for strengthening metals while limiting the dynamic recovery phenomenon.

[0003] 2. Description of the Related Art

[0004] It is possible to strengthen many metallic materials through work-hardening (sometimes called "strain hardening"). This is particularly true for materials having a face-centered cubic ("fcc") structure. Such materials form atomic matrices, where the basic unit is a cube having an atom located at each of the cube's eight corners and in the middle of each of the cube's six faces. Stainless steels, superalloys, and aluminum alloys can assume this structure, with iron atoms as the corners and the faces of the cube.

[0005] The cubic structure only remains uniform within a particular region, often called a "grain." Thus, when viewed on a microscopic level, a piece of fcc metal is comprised of many interlocking grains. Within each of these grains is a relatively uniform fcc matrix.

[0006] Plastically deforming a metal introduces dislocations into its crystalline structure. These generally tend to make the material harder and stronger. A typical example is drawing rod-shaped metal samples into smaller and smaller wires. The drawing process creates strain hardening. As the strain hardening increases, the ultimate tensile strength ("UTS") increases. Drawing high-carbon steel in this fashion produces "piano wire," which has a much higher UTS than unworked steel.

[0007] It is generally desirable for a strain-hardened piece of material to remain in the strain-hardened state. This depends upon the retention of the dislocations added to the material. For most materials, retention of the strain hardening is not an issue. However, some materials experience a phenomenon known as "dynamic recovery." When this occurs, added dislocations are "undone" over time. The material lapses partially or fully back into its undeformed state, thereby destroying the desirable effects of strain hardening. Copper is a good example of a material which exhibits dynamic recovery.

[0008] Those skilled in the art will know that copper and its alloys have been used for many years in many electrical devices. In the design of such devices, one must consider the mechanical strength of the conducting material and its conductivity. These considerations are often in opposition. Pure copper is relatively weak and ductile. It can be strengthened by adding other alloying elements. However, the addition of such elements reduces its conductivity significantly.

[0009] Pure copper can also be strengthened by strain hardening. This process reduces the copper's conductivity moderately. However, the strength achievable is limited due to the dynamic recovery phenomenon. A method of strain hardening copper while reducing the effect of the dynamic recovery phenomenon would therefore be desirable.

BRIEF SUMMARY OF THE PRESENT INVENTION

[0010] The present invention comprises a process for increasing the strength of pure copper and other fcc matrix alloys. The method is particularly applicable to face-centered-cubic materials that undergo dynamic recovery when strain-hardened at room temperature. A cryogenic strain hardening process is used to create a high strength pure copper or copper+Al_2O_3 alloy. The strength of the material is substantially increased. However, the loss of conductivity is minimal.

[0011] In the preferred embodiment, pure copper or a copper alloy is drawn into a wire at a temperature of about 77 K. Dynamic recovery of the material is substantially reduced. With this method, drawn copper wire exhibits a strength level about 45% higher than that achievable by an equivalent room temperature deformation.

[0012] The inventive method attains high strength through the stable accumulation of very high dislocation densities. The work hardening rate is changed by deforming the material under cryogenic conditions. The methodology can potentially be applied to many different materials which suffer dynamic recovery and consequent low strain hardening when deformed at room temperatures.

[0013] The inventive method can also produce highly-aligned dislocations. If, as an example, the dislocations are aligned with the central axis of a copper wire, the dislocations will have a greatly-reduced effect on the wire's conductivity.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0014] FIG. **1** is a comparison of strain hardening for two copper materials deformed at room temperature.

[0015] FIG. **2** is a comparison of the stress-strain curves for the same material deformed at room temperature and under cryogenic conditions.

[0016] FIG. **3** is a comparison of the strain hardening rates for the same material deformed at room temperature and under cryogenic conditions.

[0017] FIG. **4** is an elevation section view showing the use of a diameter reducing die to strain harden a material under cryogenic conditions.

[0018] FIG. **5** is an elevation view, showing the use of reels to pass material through a diameter reducing die.

[0019] FIG. **6** is an elevation view, showing an alternate embodiment of the device shown in FIG. **5**.

[0020] FIG. **7** is a graphical depiction of the grain boundaries within a strain-hardened sample.

[0021] FIG. **8** is a graphical depiction of the grain boundaries within a strain-hardened sample made according to the present invention.

REFERENCE NUMERALS IN THE DRAWINGS

[0022]

10	grain	12	grain boundary
14	wire axis	16	cryostat
18	wire	20	cryogenically deformed wire
28	liquid nitrogen	30	deformation zone
32	ambient atmosphere	34	draw reel
36	payoff reel	40	idler pulley

DETAILED DESCRIPTION OF THE INVENTION

[0023] The present invention contemplates strain hardening materials under cryogenic conditions. Those skilled in the art will know that strain hardening can be produced by virtually any device which plastically deforms a sample of material. Strain hardening devices include rolling mills, punches, breaks, roll formers, and drawing dies.

[0024] One familiar example of strain hardening is drawing a metal wire through a diameter reducing die (a "wire drawing die"). Such a dies plastically deforms the wire to a smaller diameter. A series of such dies can produce progressively smaller and smaller diameters.

[0025] The present inventive method uses conventional strain hardening devices. However, both the strain hardening device and the material being strain hardened are immersed in a bath of cryogenic liquefied gas during the strain hardening process. This approach is used to reduce the dynamic recovery phenomenon in face-centered-cubic materials.

[0026] The cryogenic deformation process is well suited to the creation of strain hardened conductive wires. It can be used to create a high strength pure copper conductor, a copper alloy conductor made with copper+Al_2O_3, and other materials.

[0027] The copper material is preferably strain hardened at a temperature of about 77 K (the approximate temperature of liquid nitrogen boiling at atmospheric pressure). Once the strain hardening is performed, the drawn material is allowed to return to room temperature.

[0028] The process has been used for a drawn pure copper wire of having a diameter of 3 mm. The resulting strength was 580 MPa while still retaining a conductivity of more than 96% IACS (International Annealed Copper Standard). This strength level is about 45% higher than that achievable by an equivalent room temperature deformation of copper. The material had a strength level of 680 MPa at 77 K and the resistivity ratio was larger than six.

[0029] The use of strain hardening at cryogenic temperatures is believed to: (1) produce a stable accumulation of very high dislocation densities; (2) increase the work hardening rate; and (3) alter the microstructure (as will be explained in more detail subsequently).

[0030] The process is particularly suitable for strengthening pure copper and copper matrix materials. These materials can be used as electrical conductors in many areas, such as high field pulsed magnets, high efficiency motors, and medical sensors. The process achieves the increase in strength without significantly reducing conductivity.

[0031] FIG. **1** is a plot of strain hardening characteristics for two copper samples worked at room temperature. The copper samples are C10C100 and UNS-C15715. C10100 is 99.99% pure copper (by weight). UNS-C15715 is a Cu+Al_2O_3 alloy. The unalloyed strength of the copper is increased in UNS-C15715 by the aluminum oxide dispersion in the existing copper matrix.

[0032] Both the pure copper and the aluminum oxide dispersion-strengthened copper were strain hardened at room temperature (295 K). For the pure copper (C10100), no further strain hardening occurred after a pure strain of about 1.5. The UNS-C15715 sample can be further strain hardened. Pure copper can be strain hardened at room temperature to a strength level of about 450 MPa. UNS-C157115 can be strain hardened at room temperature to about 580 MPa.

[0033] In order to achieve higher strength one would naturally seek to increase the deformation strain. However, when this is done at room temperature, the rate of change in the strain hardening ($d\sigma/d\epsilon$) approaches zero. This occurs because fcc metals (such as copper) exhibit dynamic recovery beyond a certain amount of strain. For fcc metals strengthened with alloying elements the rate of change in the strain hardening remains greater than zero, but it is very small.

[0034] FIG. **2** shows the stress-strain curve for UNS-C15760 (another aluminum oxide dispersion-strengthened copper). The lower curve reflects strain hardening conducted at room temperature. The upper curve represents strain hardening conducted at 77 K. The reader will observe how the room temperature curve flattens, while the upper curve continues to increase in strength for increasing strain.

[0035] FIG. **3** shows a comparison of the strain hardening rate of UNS-C-15760 for strain hardening performed at room temperature versus strain hardening performed at 77 K. The upper curve represents the 77K sample and the lower curve represents the room temperature sample. The reader will observe how the strain hardening rate is significantly increased for the sample hardened at 77 K.

[0036] From FIGS. **1** through **3**, one may conclude that the application of strain hardening in a cryogenic environment has significant advantages. If the deformation is performed at cryogenic temperatures, much higher flow stress levels and a significantly higher strain hardening rate can be achieved.

[0037] FIGS. **2** and **3** refer to an aluminum oxide strengthened copper. In the region above about 800 MPa (for the 77 K sample), dislocation accumulation occurs due to the presence of the nano-scale alumina particles. This accumulation promotes the formation of sub-grains or even nano-grains in the copper. In-face sub-grains on the scale of 100 nm have been observed in the pure copper deformed at 77 K.

[0038] At a stress of 800 MPa, the material hardens at a rate of approximately 2000 MPa (strain being unit less). This strain hardening rate is approximately G/16, where G is the shear modulus of copper (about 33 GPa). For room temperature strain hardening, the rate is only about G/200. Thus, cryogenic deformation produces a drastic change in the material properties, with a significant increase in the strain hardening rate. The result is that a much higher UTS can be obtained using less strain.

[0039] Impurities introduced into copper often reduce the conductivity of the resulting alloy in comparison to pure copper. Impurities can change the resistivity by a factor of two per 1% of added impurity. Using the present cryogenic strain hardening process for pure copper or copper dispersion-strengthened by aluminum oxide only introduces dislocations. It does not produce a dissolution of any second phase, such as the aluminum oxide. Therefore, the decrease in conductivity resulting from the cryogenic strain hardening process is mainly due to dislocation accumulation.

[0040] This fact allows the change in resistivity to be used to calculate an estimation for dislocation accumulation. The resistivity of pure copper cryogenically drawn to a strain of 2.3 is $1.79\times10^{-8}\Omega\cdot m$ (at room temperature). This figure represents only about a 4% increase over the resistivity of pure annealed copper. Therefore, although the cryogenic drawing process increases the strength considerably, the increase in resistivity is minimal.

[0041] Now that the reader understands the advantages of the cryogenic strain hardening process, devices used to implement the process will be discussed. The following examples are intended to illustrate the broad concepts of such devices, with the understanding that many variations are possible.

[0042] FIG. **4** is a sectional elevation view through a cryostat **16** containing liquid nitrogen **28**. The term "cryostat" will be understood to encompass any vessel capable of containing a cryogenic liquefied gas. Vessels using a Dewar-type evacuated wall construction work well in this application, but other constructions are possible.

[0043] The liquid nitrogen is vented to the atmosphere, resulting in the maintenance of its boiling temperature of about 77 K. An fcc metal is placed in the cryostat along with the strain-producing device. In the particular example shown, a copper or copper alloy wire **18** of a first diameter is placed within the vessel. It is forced through a diameter reducing die **22** which draws it down to a second reduced diameter as the wire passes through deformation zone **30**. Cryogenically deformed wire **20** remains in the liquid nitrogen for some period before exiting the cryostat and returning to ambient atmosphere **32**. Thus, the strain hardening occurs at cryogenic temperatures.

[0044] Those skilled in the art will realize that the device illustrated in FIG. **4** is not very practical. Wire drawing operations generally involve long lengths of wire, requiring the use of drums or spools to maintain desirable tension. FIG. **5** shows an elevation view of a more sophisticated device. A liquid nitrogen cryostat **38** is used to house payoff reel **36**. It pays out copper wire of a first diameter. The wire is drawn through a wire drawing die **22** as before (The die is also immersed in the liquefied gas contained within the cryostat. The wire is then taken up on the rotating draw reel **34**, which also applies tension.

[0045] The top of the cryostat is depicted as being open, though in reality it would need to be mostly sealed in order to prevent an inordinately high boil-off rate. The drawn wire would likely exit the cryostat through a small opening through a well insulated wall.

[0046] FIG. **6** shows an alternate embodiment in which the payoff reel and draw block are both located outside the cryostat. Two submerged "idler" pulleys **40** are preferably used to maintain tension on the wire as it passes through the cryostat. However, the larger payoff reel and draw reel remain outside the cryostat. This fact means that the cryostat can be smaller and that the payoff reel and draw reel do not need to be designed to withstand the extremely low temperatures found in the cryostat. As for the embodiment of FIG. **5**, the top of the cryostat shown in FIG. **6** would actually be closed with only small openings provided for the passage of the wire.

[0047] FIGS. **7** and **8** illustrate some of the grain properties of the deformed fcc materials and serve to explain some of the advantages obtained by performing the present inventive method. FIG. **7** shows a graphical depiction of the grain boundaries in a strain-hardened fcc metal. The image is a cross sectional view, with the section being transverse to the direction in which the metal was drawn. The left hand view shows a sample which was drawn at room temperature ("RT Sample"), whereas the right hand view shows a sample which was drawn under cryogenic conditions ("LNT Sample") using the present process.

[0048] The RT Sample shows elongated cells, which are a result of dynamic recovery after the strain hardening. The LNT Sample, in contrast, shows cells having a generally circular cross section. A cell size for the LNT Sample is about 150 nm, whereas a cell size for the RT Sample is about 190 nm. The LNT Sample shows more variation in cell size, which again is a result of the reduction in the dynamic recovery phenomenon. Such microstructure differences contribute to the property differences between the two types of samples.

[0049] FIG. **8** shows another graphical depiction of the grain structure in an fcc metal sample, with the section this time being taken in the same plane as the direction in which the metal was drawn. The reader will observe how the dislocations are highly oriented, generally aligning with the direction of drawing.

[0050] Although the preceding description contains significant detail, it should not be construed as limiting the scope of the invention but rather as providing illustrations of the preferred embodiments of the invention. As an example, although copper and copper alloys have been discussed in the descriptions, the inventive method could be applied to other fcc metals which exhibit dynamic recovery. The inventive process could likewise be carried out in many different ways. As an additional example, sheet material could be fed through a small rolling mill (which would reduce the sheet thickness and increase its width) contained in a cryostat. The rolling mill would be the strain producing device and would be equivalent to the drawing dies shown in the illustrations. Thus, the scope of the invention should be fixed by the following claims rather than the examples given. The inventors acknowledge the helpful discussion provided by Dr. J. D. Embury.

[0051] Having described our invention, we claim:

1. A method for strain hardening a length of metal while reducing dynamic recovery, comprising:
- a. providing a vessel containing a cryogenic liquefied gas;
- b. providing a deformation die, located within said vessel and immersed in said cryogenic liquefied gas; and
- c. passing said length of metal through said deformation die while a portion of said length of metal proximate said deformation die and said deformation die remain immersed in said cryogenic liquefied gas.

2. A method of strain hardening as recited in claim **1**, wherein said cryogenic liquefied gas is liquid nitrogen.

3. A method of strain hardening as recited in claim **1** wherein said length of metal is a wire and said deformation die is a diameter reducing die.

4. A method of strain hardening as recited in claim **3**, wherein said wire is fed from a payoff reel, through said diameter reducing die, and onto a draw reel.

5. A method of strain hardening as recited in claim **4**, wherein said payoff reel is contained within said vessel and said draw reel is located outside said vessel.

6. A method of strain hardening as recited in claim **4**, wherein both said payoff reel and said draw reel are located outside said vessel.

7. A method of strain hardening as recited in claim **6**, wherein said wire is fed from said payoff reel to a first idler pulley, then through said diameter reducing die, then to a second idler pulley, and then to said draw reel.

8. A method of strain hardening as recited in claim **7**, wherein said first and second idler pulleys are contained within said vessel.

9. A method for strain hardening a length of metal while reducing dynamic recovery, comprising:
- a. providing a volume of cryogenic liquefied gas;
- b. providing a deformation die;
- c. immersing said deformation die in said volume of cryogenic liquefied gas; and
- d. using said deformation die to deform said length of metal while a portion of said length of metal proximate said deformation die and said deformation die remain immersed in said cryogenic liquefied gas.

10. A method of strain hardening as recited in claim **9**, wherein said cryogenic liquefied gas is liquid nitrogen.

11. A method of strain hardening as recited in claim **9** wherein said length of metal is a wire and said deformation die is a diameter reducing die.

12. A method of strain hardening as recited in claim **11**, wherein said wire is fed from a payoff reel, through said diameter reducing die, and onto a draw reel.

13. A method of strain hardening as recited in claim **12**, wherein said payoff reel is contained within said vessel and said draw reel is located outside said vessel.

14. A method of strain hardening as recited in claim **12**, wherein both said payoff reel and said draw reel are located outside said vessel.

15. A method of strain hardening as recited in claim **14**, wherein said wire is fed from said payoff reel to a first idler pulley, then through said diameter reducing die, then to a second idler pulley, and then to said draw reel.

16. A method of strain hardening as recited in claim **15**, wherein said first and second idler pulleys are contained within said vessel.

17. A method of strain hardening as recited in claim **3**, wherein said cryogenic liquefied gas is liquid nitrogen.

18. A method of strain hardening as recited in claim **4**, wherein said cryogenic liquefied gas is liquid nitrogen.

19. A method of strain hardening as recited in claim **11**, wherein said cryogenic liquefied gas is liquid nitrogen.

20. A method of strain hardening as recited in claim **12**, wherein said cryogenic liquefied gas is liquid nitrogen.

* * * * *